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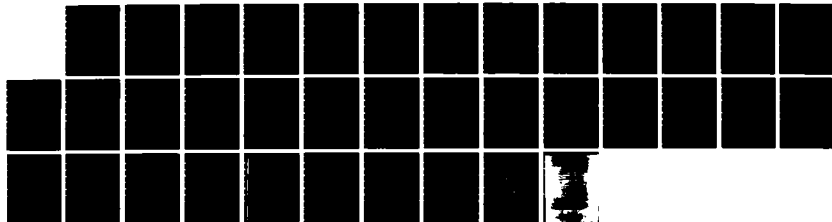
THERMAL DEGRADATION STUDIES OF SEGMENTED THERMOPLASTIC
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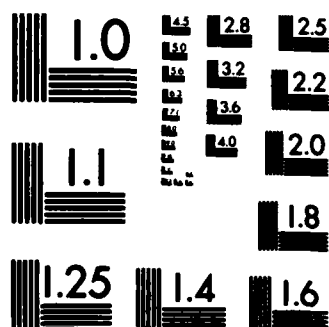
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TECHNICAL REPORT NO. 2

THERMAL DEGRADATION STUDIES OF
SEGMENTED THERMOPLASTIC ELASTOMERS

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Thermal Degradation Studies of Segmented Thermoplastic Elastomers

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Abstract

Pyrolysis-gas chromatography (GC) - mass spectrometry (MS) have been performed on several thermoplastic elastomers. The soft blocks are hydroxy terminated polypropylene oxide (PPO, MW = 2000) and polyacetal of butyraldehyde and diethylene glycol (PA, MW = 1500). The hard blocks were introduced by reacting the soft block polymers with 4,4'-diphenylmethane diisocyanate (MDI) chain extended with butanediol, pentanediol, and N,N'-bis(2-hydroxyethyl)isophthalamide to form the respective polyurethanes and with pyromellitic anhydride to give the polyimide. Most of the pyrolysates of the soft segments can be accounted for by the thermolysis of any single backbone bond into various macroradicals and elimination of observed compounds by either intramolecular hydrogen, methyl shift, or ring closure. Certain other products were better explained by direct intramolecular rearrangements. These processes are believed to be much more probable according to energetic considerations than two bond fragmentation followed by multiple hydrogen abstraction or elimination. Pyrograms do not show any products which may result from coupling or disproportionation of such fragments. The hard segment pyrolysates were probably also formed by intra-

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molecular rearrangements. In the case of PPOPU-BI, pyrolysis at 300°C yielded only products from the hard blocks. Subsequent pyrolysis at 550°C has the same pyrogram as hydroxy terminated PPO. Therefore, these segmented block copolymers decompose in two stages; the hard blocks thermolyze first followed by thermolysis of the soft blocks in agreement with previous TGA results.

INTRODUCTION

We have undertaken a systematic study of structure-property relationships of segmented thermoplastic elastomers. These polymers contain alternating blocks of soft segments, \underline{S} , and hard segments, \underline{H} , which can be represented by $[\underline{S}_a \underline{H}_b]_n$. The hard segments can be amorphous (but with T_g much higher than room temperature) or are semicrystalline. If the structures of \underline{S} and \underline{H} segments differ greatly, i.e., polarity, and highly incompatible or \underline{H} segments form a crystalline domain, then there is microphase separation. The hard domains act as physical crosslinks for the elastomeric \underline{S} domains. Yet above T_g or T_m of the \underline{H} domains the physical crosslinks become very weak or ineffective and the material can be processed as thermoplastics.

In this investigation we have used for \underline{S} blocks either poly(propylene oxide) (PPO) or polyacetal (PA), both with terminal hydroxyl groups; the \underline{H} blocks contain either polyurethanes (PU) from the reactions of diisocyanates with diol chain extenders or polyimide (PI) from the reactions of diisocyanates with dianhydrides. These polymers have different thermal transition and mechanical properties. The purpose of this work is to identify their pyrolysis products with GC-MS in order to elucidate their

thermal decomposition mechanisms.

EXPERIMENTAL

Soft segments

Hydroxy terminated PPO (MW = 2000) was obtained from Polysciences. Polyacetal with terminal hydroxyls was obtained¹ by toluene sulfonic acid catalyzed polymerization of diethylene glycol and n-butyraldehyde from Aldrich to MW \approx 1500. The hydroxyl groups were determined by the Karl Fischer method.

Hard segment components

4,4'-Diphenylmethanediisocyanate (MDI) from Mobay Chemicals was distilled under reduced pressure and stored in a brown wide-mouthed jar under argon at -4°C . N,N'-Bis(2-hydroxyethyl)isophthalamide (BI) was synthesized by aminolysis of the isophthalate esters using 2-aminoethanol. Pentanediol (P) and butanediol (B) was purchased from Aldrich and distilled before use. Pyromellitic anhydride (PMDA), Aldrich, was either crystallized from acetic anhydride or purified by sublimation.

Synthesis of segmented block copolymers

The polymers studied in this work are given in Table I.

The segmented block copolymers were synthesized by a two-stage process.² The hydroxy terminated soft segment was first capped by an appropriate amount of MDI at $60-70^{\circ}\text{C}$ in the presence of dibutyltin dilaurate (0.5% by weight). Then chain extender was added, and chain extension was allowed to proceed at room temperature for 4 hrs in DMF solution. The reaction was terminated by the addition of methanol. The solvent was removed by evaporation, and the product was dried at $60-70^{\circ}\text{C}$ for 48 hrs under high

vacuum. Full characterization results of the polymers are given elsewhere.²

TABLE I. Synthesis of Thermoplastic Elastomers

Polymer	Soft segment (mole)	MDI (mole)	Chain extender (mole)
PPOPU-2-5-3-P	PPO (2)	(5)	P (3)
PPOPU-1-2-1-BI	PPO (1)	(2)	BI (1)
PPOPU-1-3-2-BI	PPO (1)	(3)	BI (2)
PPOPI-1-2-1-PDMA	PPO (1)	(2)	PDMA (1)
PAPU-1-2-1-BI	PA (1)	(2)	BI (1)
PAPU-1-2-1-B	PA (1)	(2)	B (1)

Pyrolysis-GC-FID³

About 100-500 μ g samples of the thermoplastic elastomers were weighed on a Fisher microbalance. The polymer was then placed in a quartz tube which was inserted into the platinum coil probe of the CDS pyrolysis interface which had an injection needle insert connected to a Varian 3700 gas chromatograph. After purging with helium for 10 minutes, the sample was pyrolyzed at an appropriate temperature for 20 seconds in helium and the pyrolysates were separated gas chromatographically.

Three columns were used to separate the pyrolysates. A Chromosorb 102 (John Manville Corp., Denver, CO) packed column (60/80 mesh, 6' x 1/8" o.d.) was used to separate low-boiling compounds. The column temperature was

programmed from 40°C to 230°C at 8°C/min; the flow rate of the helium carrier gas was 30 mL/min. For higher-boiling products a SE-30 fused silica capillary column (13m x 0.32mm i.d., J & W Scientific Co., Rancho Cordova, CA) was employed, programmed from 40°C to 225°C at 5°C/min. The helium flow rate was 2 mL/min and the inlet split ratio was 30:1. The flow rate of helium makeup gas was 30 mL/min. Pyrolysis products were detected by flame ionization.

A Carbowax-20M fused silica capillary column (50m x 0.28mm i.d., J & W Scientific Co., Rancho Cordova, CA) was used to separate the polar compounds. The column temperature was programmed from 40°C to 200°C at 5°C/min.

Pyrolysis-GC-MS

The low-boiling pyrolysates were identified by a Hitachi MRU-6L mass spectrometer interfaced with a Perkin-Elmer 990 gas chromatograph by a jet separator. In order to obtain unequivocal mass spectrum for each pyrolysis product, the sample size was increased to about 2.5 mg for each run.

The eluted high-boiling pyrolysis products were characterized by a Hewlett-Packard model 5985A quadrupole mass spectrometer coupled with a 5840A gas chromatograph by a Pt-Ir transfer line for the capillary column investigation. A Hewlett-Packard model 2648A data system was used to aid in interpretation of mass spectra.

RESULTS & DISCUSSION

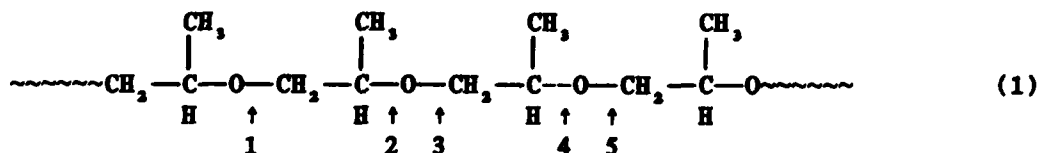
To simplify data analysis of the thermoplastic elastomers, the pyrolysis of the soft segments were investigated first. These products can then be largely ignored in analyzing the pyrolysates of the segment block

copolymers derived from the hard segments or the atoms linking the two kinds of segments.

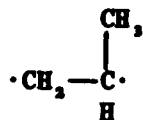
Poly(propylene oxide)

PPO was flash pyrolyzed at 600°C in He for 20 sec. Figure 1 shows the pyrogram. The main eluents were identified by MS and summarized in Table II.

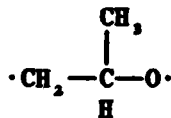
A simple minded interpretation of the mechanism pyrolysis would be the random fragmentation of the backbone followed by hydrogen abstraction or hydrogen elimination. For illustrative purposes many of the most abundant products might be derived from the fragments by breaking the indicated pairs of backbone bonds.



Breaking of bonds at 1 and 2 gives

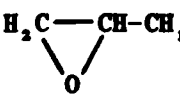
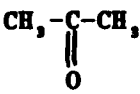
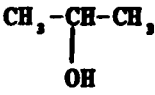
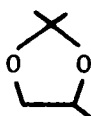
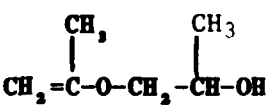
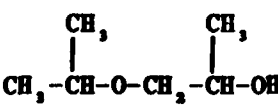
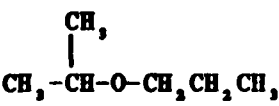


or propylene; abstraction of two hydrogen atoms can form propane. The



fragments derived from scission at 1 and 3 can rearrange to give acetone, ring closing to form propylene oxide, or abstraction of two hydrogen atoms to give isopropanol. Scission at 1 and 4 followed by abstraction of two

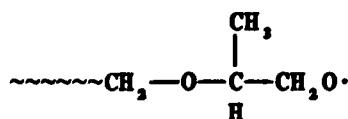
TABLE II. Low-Boiling Products of the Pyrolysis of PPO in Helium

Peak Number	Pyrolysis Products
1	CO
2	CH ₄
3	C ₂ H ₄
4	C ₂ H ₆
5	H ₂ O
6	C ₃ H ₆
7	C ₃ H ₈
8	CH ₃ CHO
9	
10	
11	CH ₃ CH ₂ CHO
12	
13	CH ₃ CH ₂ CH ₂ OH
14	
15	
16	
17	

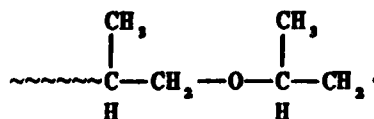
hydrogen atoms can produce the observed propyl-*i*-propyl ether (peak 17). Finally, the diradical resulted from scission at 1 and 5 positions followed by hydrogen migration or abstraction may account for products 15 and 16 of Table II.

There are two main objections to the direct fragmentation of backbone. These simultaneous processes involve two bonds with energies in excess of 120 kcal mole⁻¹ and therefore even greater energies of activation. Even at 600°C an exponential term of 10⁻³⁰ cannot be overcome by any reasonable pre-exponential factor to give a significant rate constant. Secondly, more energy would be required for subsequent abstraction of hydrogen atoms and one would expect products, for instance isomeric C₄-C₆ alkanes, alkenes and alkadienes, etc. In the case of flash pyrolysis of polypropylene^{4,5} and polyisoprene,^{6,7} we accounted for all the products by single main chain scission followed by intramolecular hydrogen shifts. Flash pyrolysis products of polyacetylene^{8,9} and of polymethylacetylene^{9,10} were interpreted as the results of main chain scission accompanied by electron-proton exchange and electron-methyl exchange processes.

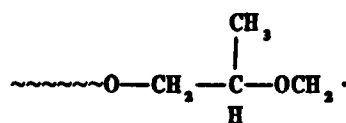
The probable pyrolysis reaction pathways for PPO may be postulated to proceed according to the scission of simple backbone bonds followed by some rearrangement processes of the resulting radicals. Random chain scission can produce six different macroradicals I to VI:



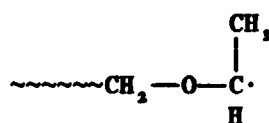
(I)



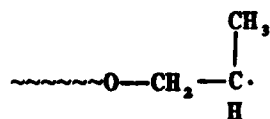
(II)



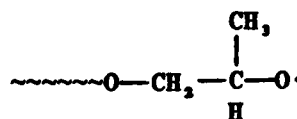
(III)



(IV)



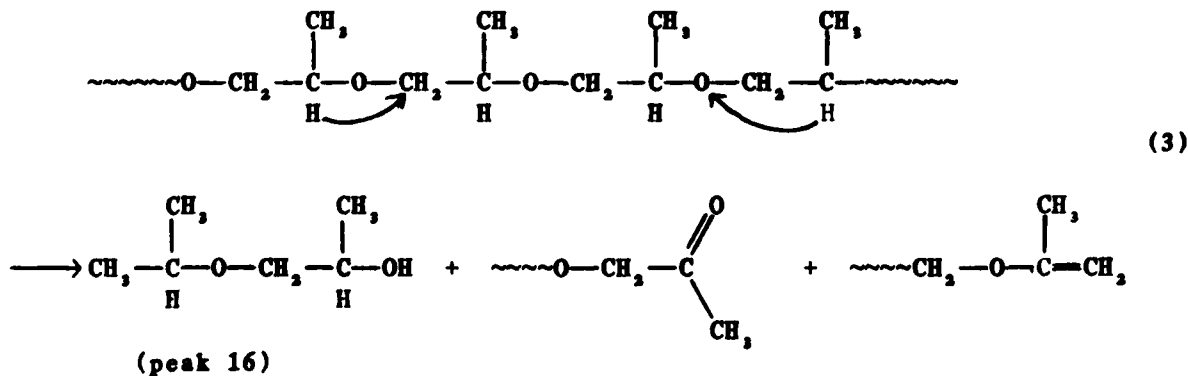
(V)

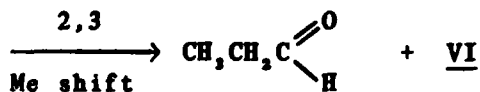
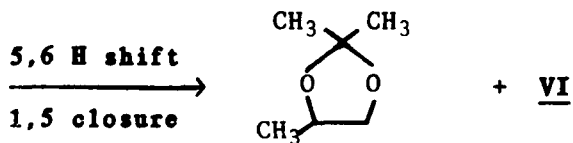
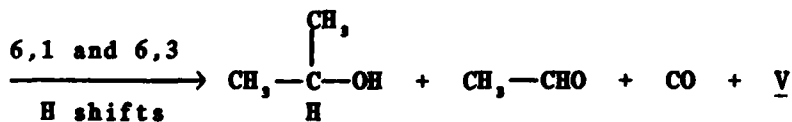
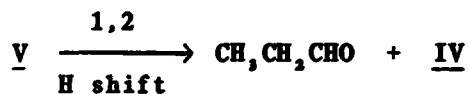
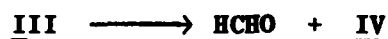
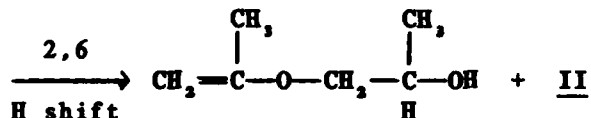
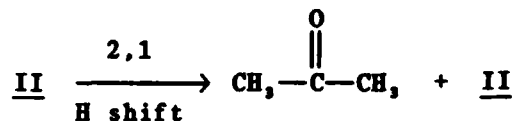
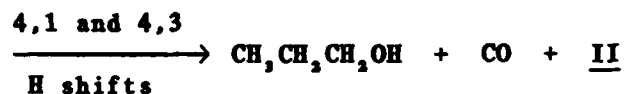


(VI)

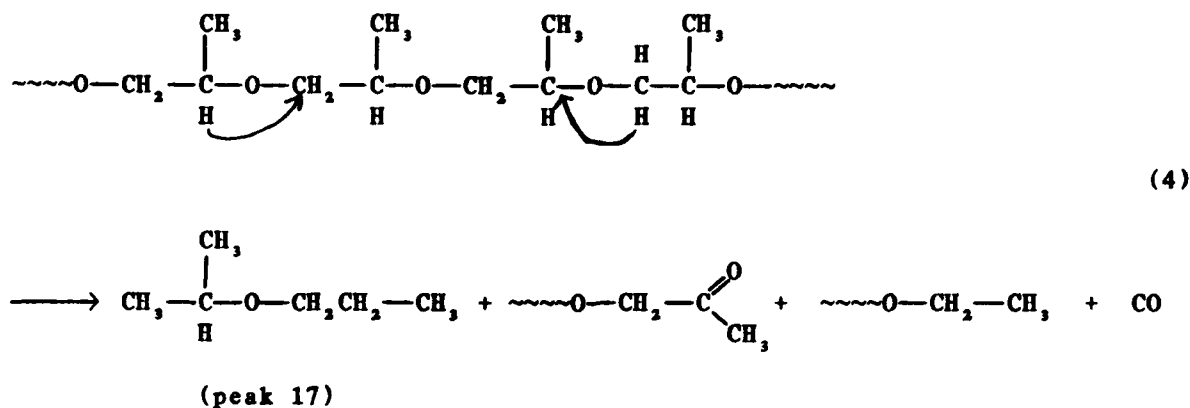
In the subsequent rearrangement, the H or CH₃ shifts are indicated by two numbers, the shift being from the first numbered atom to the second. Similarly, for ring closures the two numbers designate the atoms involved in the cyclization. Most of the major products in Table II can be rationalized by the low energy rearrangement processes of radicals I to VI as in Scheme I.

Two of the main products (peaks 16 and 17 of Table II) cannot be reasonably accounted for by Scheme I. Instead, they may be formed by direct scission of backbone via molecular rearrangements of hydrogen shifts indicated by the arrows:





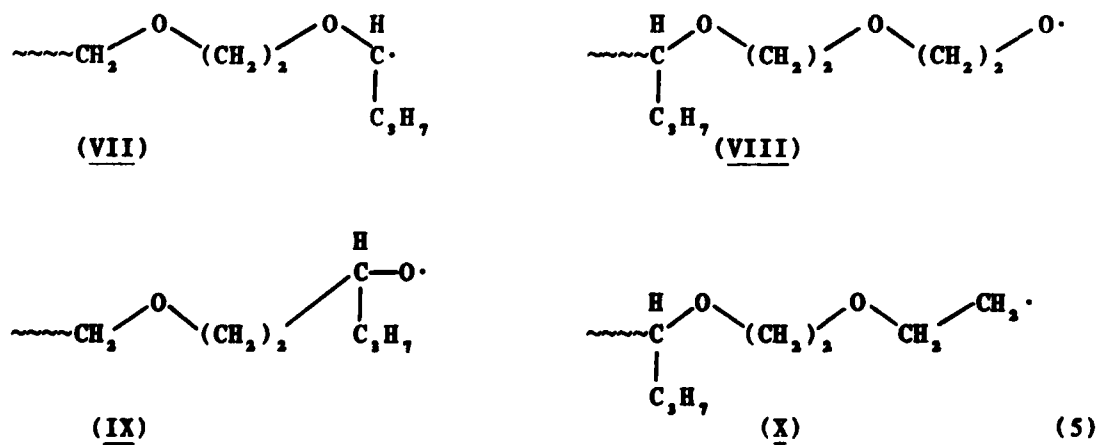
SCHEME I. Possible mechanisms for pyrolysis of PPO.

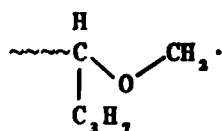


In addition, scission of the CH_3 group can result in the minor products CH_4 and C_2H_6 . Finally, radicals I to VI can all eliminate propylene oxide regenerating the corresponding parent radical. However, the formation of the strain ring compound is unfavorable and only a very small amount of it was detected.

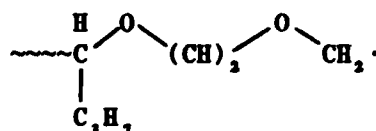
Polyacetal

The flash pyrolysis pyrogram of PA is shown in Figure 2. The products identified by MS are given in Table III. For the same reasons as given above for PPO, we consider the random scission of backbone to produce the following macroradicals:

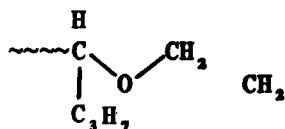




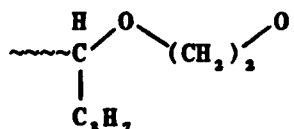
(XI)



(XII)



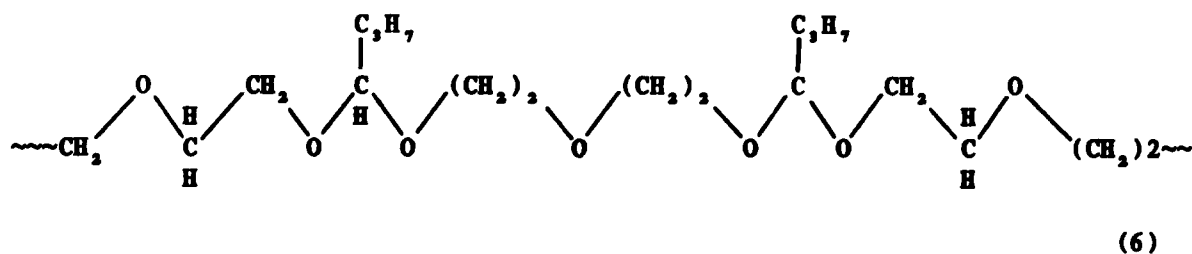
(XIII)



(XIV)

Most of the observed products can be formed by rearrangement of these radicals such as those in Scheme II.

In the above rearrangement of Scheme II, the primed numbers are for the propyl pendant group. Analogous reactions occur for radicals XI to XIV to give the same products. However, it is difficult to propose a mechanism for the formation of diethylene glycol which together with butyraldehyde are the main products. An intramolecular hydrogen shift is suggested instead;



(6)

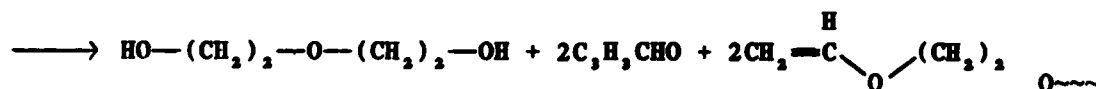
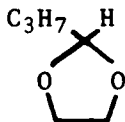
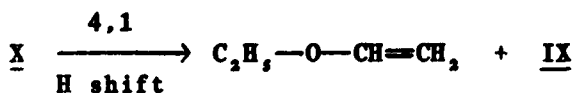
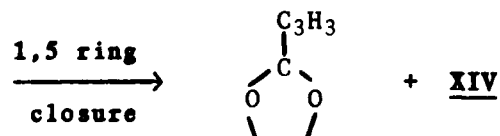
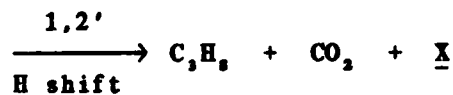
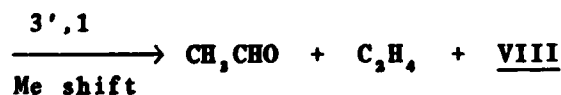
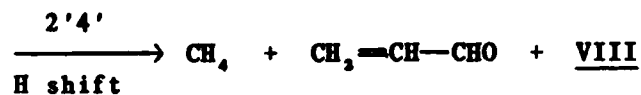
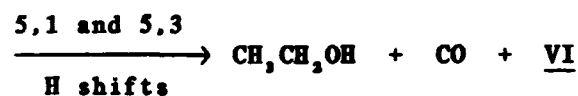
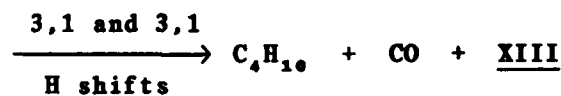
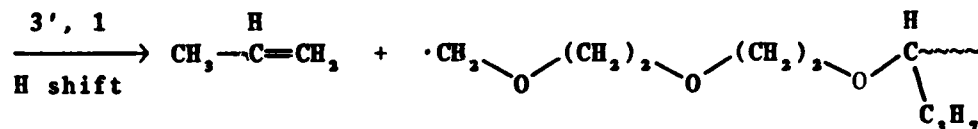
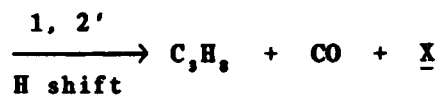
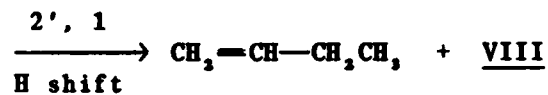
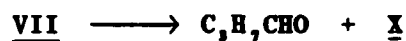


Table III. Low-Boiling Products of the Pyrolysis of Polyacetal in Helium

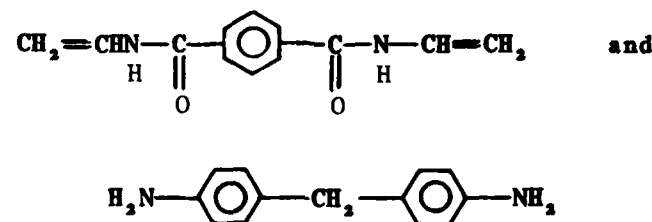
Peak Number	Pyrolysis Product
1	CO
2	CH ₄
3	CO ₂
4	C ₂ H ₄
5	C ₂ H ₆
6	H ₂ O
7	C ₃ H ₆
8	C ₃ H ₈
9	CH ₃ CHO
10	CH ₂ =CH-CH ₂ -CH ₃
11	CH ₃ -CH ₂ -CH ₂ -CH ₃
12	C ₂ H ₅ OH
13	CH ₂ =CHCHO
14	C ₂ H ₅ -O-CH=CH ₂
15	n-C ₃ H ₇ CHO
16	
17	HO-CH ₂ CH ₂ -O-CH ₂ CH ₂ -OH



SCHEME II. Possible mechanisms for pyrolysis of polyacetal.

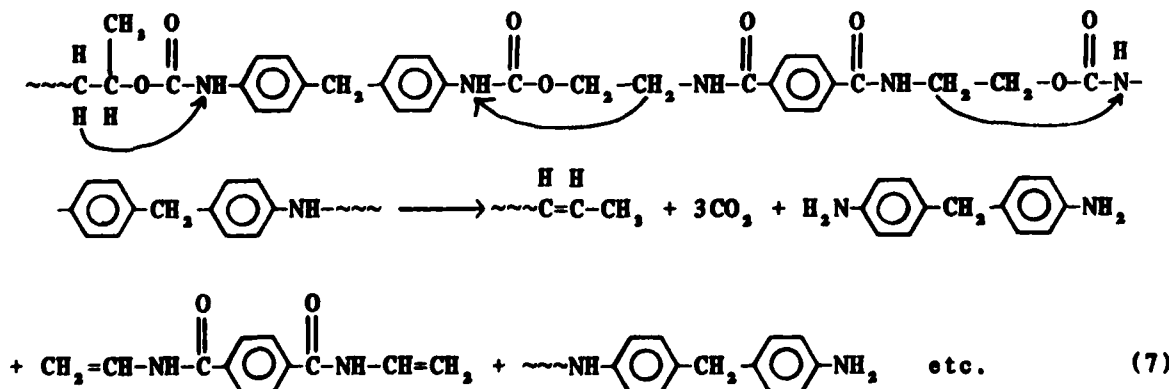
PPOPU-BI polymers

Flash pyrolysis at 500°C and 600°C for 20 sec had been carried out and GC-MS performed for the 1-2-1 and 1-3-2 thermoplastic elastomers. The low boiling fractions showed pyrograms obtained with a Chromosorb 102 column (shown in Figure 3a) which are virtually identical to those given in Figure 1a for PPO alone except for the strong new CO₂ peak designated as A. The high-boiling products chromatographed with a fused silica capillary column are shown in Figure 3b. Comparison with Figure 1b of PPO showed the decrease of yields of peaks 14 and 17, and the series of unidentified multiplets. Two new products designated as peaks 18 and 19 had been identified to be



respectively.

The new pyrolysis products of segmented block copolymers, which are absent among the pyrolysates of PPO, were obviously derived from the hard segments and the atoms linking them to the soft segments. They can be readily accounted for by the following mechanism:

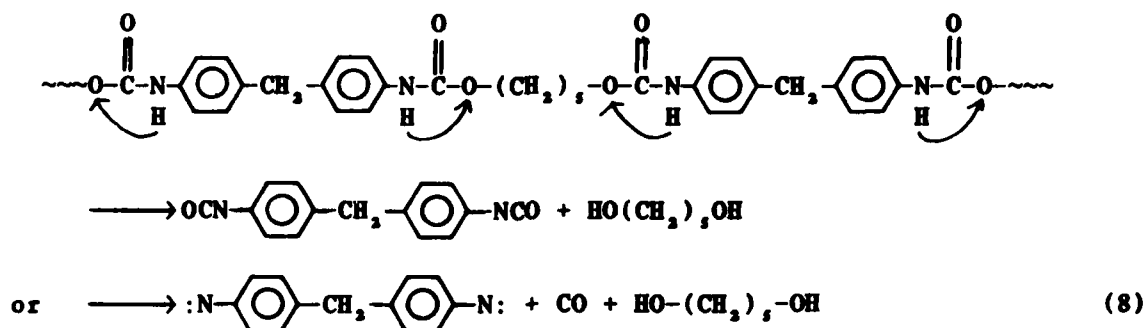


Earlier in the DSC and TGA studies of PPOPU thermoplastic elastomers,³ it was found that the hard segment decomposes before the polyether soft segment in a two-stage process. This conclusion is confirmed by the following experiment. The PPOPU-BI copolymer was first pyrolyzed at a low temperature of 330°C and the products chromatographed on a SE-30 fused silica capillary column (Figure 4a). Peaks 18 and 19 of the hard segments were clearly the dominant products. The same sample was subsequently pyrolyzed at 550°C; the two peaks disappeared in that pyrogram (Figure 4b). Therefore, the hard segments have all pyrolyzed during the first heating stage. In TGA experiments with a much slower heating rate of 20° min⁻¹, the first stage decomposition of the hard segment is complete at ca. 300°C.

PPOPU-P polymers

The pyrograms of PPOPU-2-5-3-P thermoplastic elastomers are given in Figure 5. PPOPU-P differs from PPOPU-BI in their chain extenders which are P and BI, respectively, both coupled with MDI. Comparison of pyrograms 4 and 5 showed that peaks 18 and 19 in the latter had disappeared in the former which produces a new peak due of pentanediol label B. N,N'-divinyl isophthalamide (peak 18) is due to BI and is expected to be absent. The absence of diaminophenylmethane (peak 19) and the formation of B can be attributed to the effect of greater stabilization of the O-H bond rather than the N-H bond.

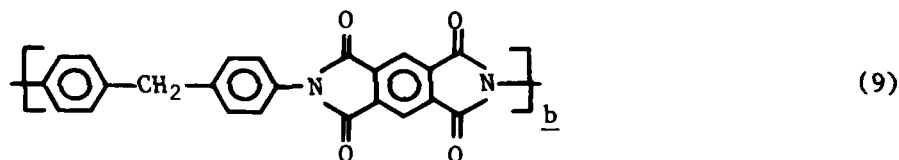
The preferred pyrolysis process for the hard segment is:



Either the nitrene or the diisocyanate probably reacts with the column packing materials and is not eluted.

PPOPI-PDMA

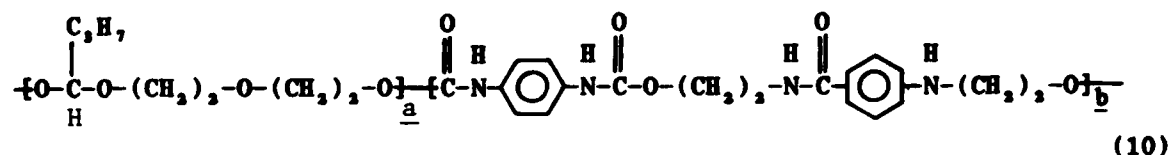
This strong thermoplastic elastomer has the following hard segment structure:



Pyrolysis of the polymer and analysis by the above described columns gave pyrograms identical to those from PPO alone (Figure 1). It was thought that the pyrolysates from the polyimide hard segment may be very polar and were adsorbed on the SE-30 fused silica column. A Carbowax 20M fused silica column was used to attempt better separation. However, Figure 6 showed identical pyrograms for PPO and the polyimide segmented block copolymers. It appears that the polyimide products are either too non-volatile or too reactive to be eluted with the present techniques.

PAPU-BI

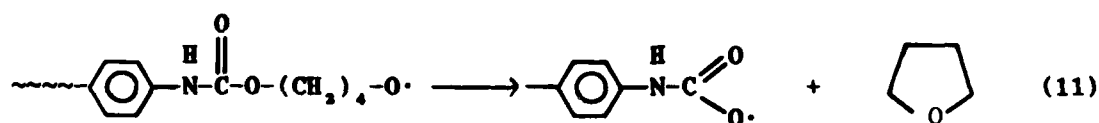
The PAPU-BI block copolymer has the following segmented structure:



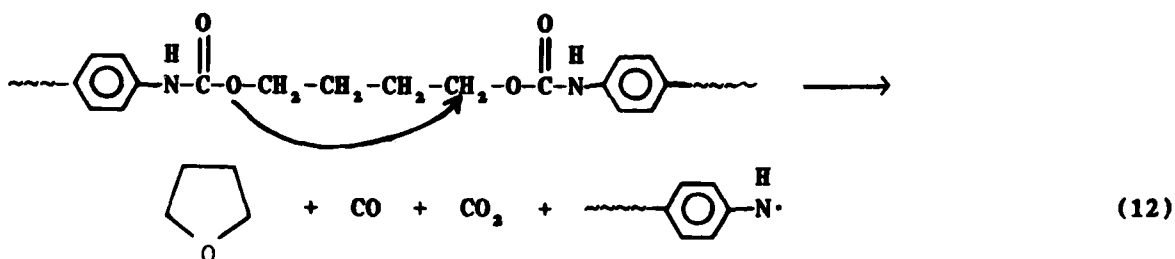
Flash pyrolysis at 550°C for 20 sec gave a low boiling pyrogram (Chromosorb 102 column) virtually identical to that of polyacetal alone (Figure 2). The only significant difference is the CO₂ peak (#3 in Table III and Fig. 2) which is increased about twelve-fold for the block copolymers. For the high boiling fraction the copolymers produced N,N'-divinylisophthalamide and diaminophenylmethane as in the case of the PPOPU-BI materials. These differences between the polyacetal and its copolymer can be explained by the reaction 7 for the hard segments.

PAPU-B

This copolymer differs from the previous one in that the chain extender is butandiol instead of bis(hydroxyethyl)isophthalamide. The Chromosorb 102 pyrogram of the pyrolysate of PAPU-1-2-1-B is given in Figure 7. Comparison with Figure 2 showed the increase of CO₂ (peak 3) by about thirteen-fold and the new peaks C and D which were found by MS to be tetrahydrofuran and butanediol, respectively. The latter product can be produced by the processes analogous to reaction 8 postulated for the pyrolysis of PPOPU-P polymer. In this instance the favored five-membered ring THF was also formed either from a macroradical



or directly from the hard segment via intramolecular rearrangement.



CONCLUSION

Flash pyrolysis of segmented thermoplastic elastomers has been performed. The products were GC separated and MS identified. Most of the products of the soft segments were accounted for by random scission of one backbone bond to give macroradicals which eliminate various compounds via intramolecular shifts of hydrogens or methyl groups and ring closure. Certain products were better rationalized by direct intramolecular rearrangements. In the case of polyetherpolyurethane chain extended with BI, it was shown that the hard segment decomposes before the soft segment in agreement with earlier TGA results. This study showed that pyrolysis-GC-MS can be used either to elucidate the mechanism of thermal decomposition of segmented block copolymers or to determine the structures of related unknown copolymers. Only in the case of the polyimide hard segment were we unable to detect its pyrolysate.

ACKNOWLEDGEMENT

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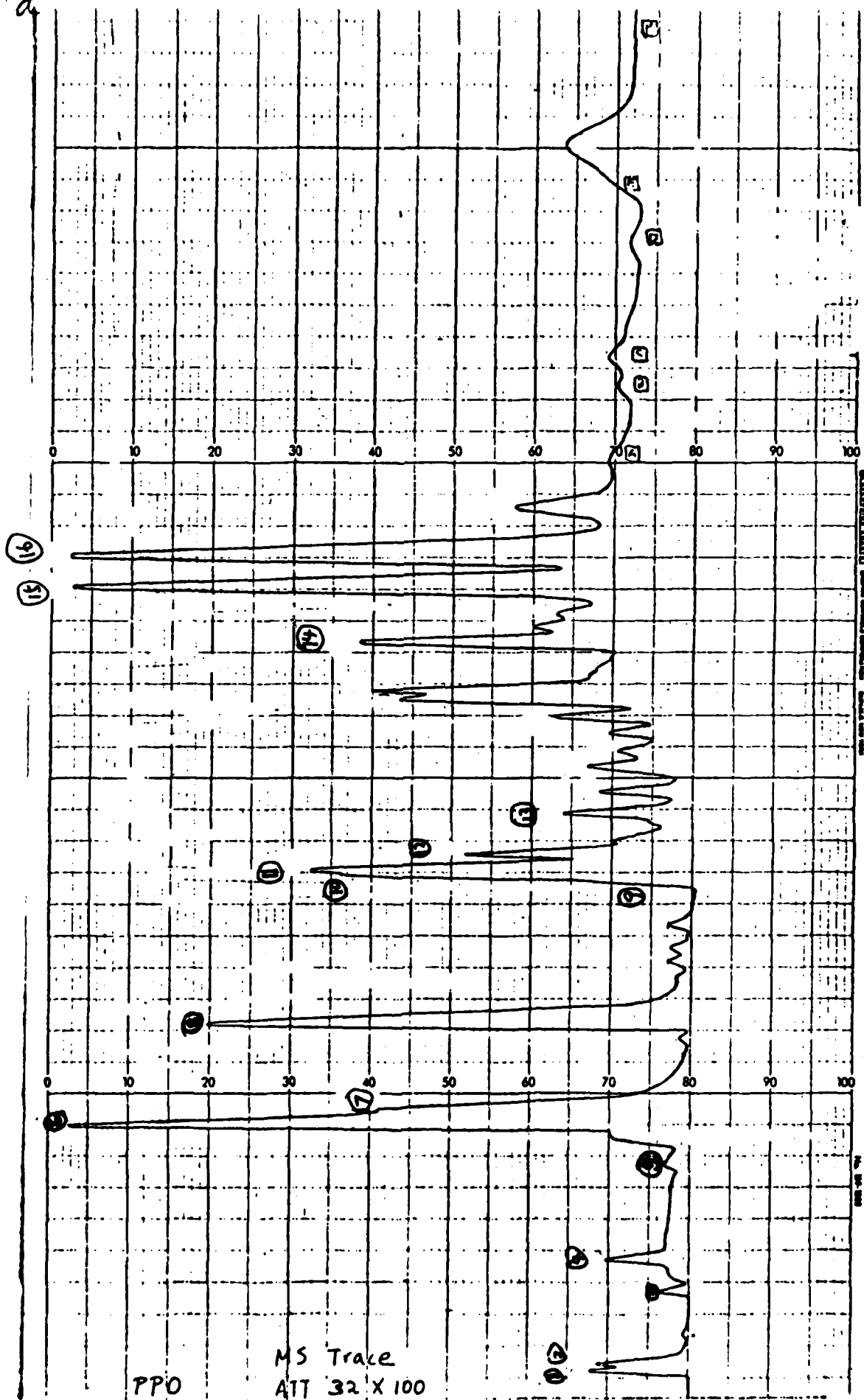
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Captions for Figures

- Figure 1. Pyrogram of PPO: (a) low boiling products separated on a Chromosorb 102 column; (b) high boiling products separated on a SE-30 fused silica capillary column.
- Figure 2. Pyrogram of polyacetal pyrolyzed at 600°C in He for 20 sec separated on a Chromosorb 102 column.
- Figure 3. Pyrogram of PPOPU-BI copolymer for both 1-2-1 and 1-3-2 composition at 600°C for 20 sec: (a) low boiling products separated on a Chromosorb 102 column; (b) high boiling products separated on a SE-30 fused silica capillary column.
- Figure 4. Pyrograms obtained with a SE-30 fused silica column from 0.34 mg of PPOPU-1-2-1-BI and the 1-3-2 polymers (a) pyrolyzed first at 330°C for 20 sec; (b) the same sample subsequently pyrolyzed at 500°C for 20 sec.
- Figure 5. Pyrograms of PPOPU-2-5-3-P copolymers at 600°C for 20 sec: (a) low boiling products; (b) high boiling products.
- Figure 6. Pyrograms of (a) PPO, MW = 2000 and (b) PPOPI-1-2-1-PDMA, both pyrolyzed at 600°C for 20 sec and separated on a Carbowax 20M fused silica capillary column.
- Figure 7. Pyrogram of PAPU-1-2-1-B pyrolyzed at 550°C for 20 sec separated on a Chromosorb 102 column.

Figure 1a

Fig 1a



PPO

Poly propylene oxide, MW=2000

pyrolyzed at 500°C in He for 20 sec

separated on a SE-30 fused silica capillary column

Figure 1b

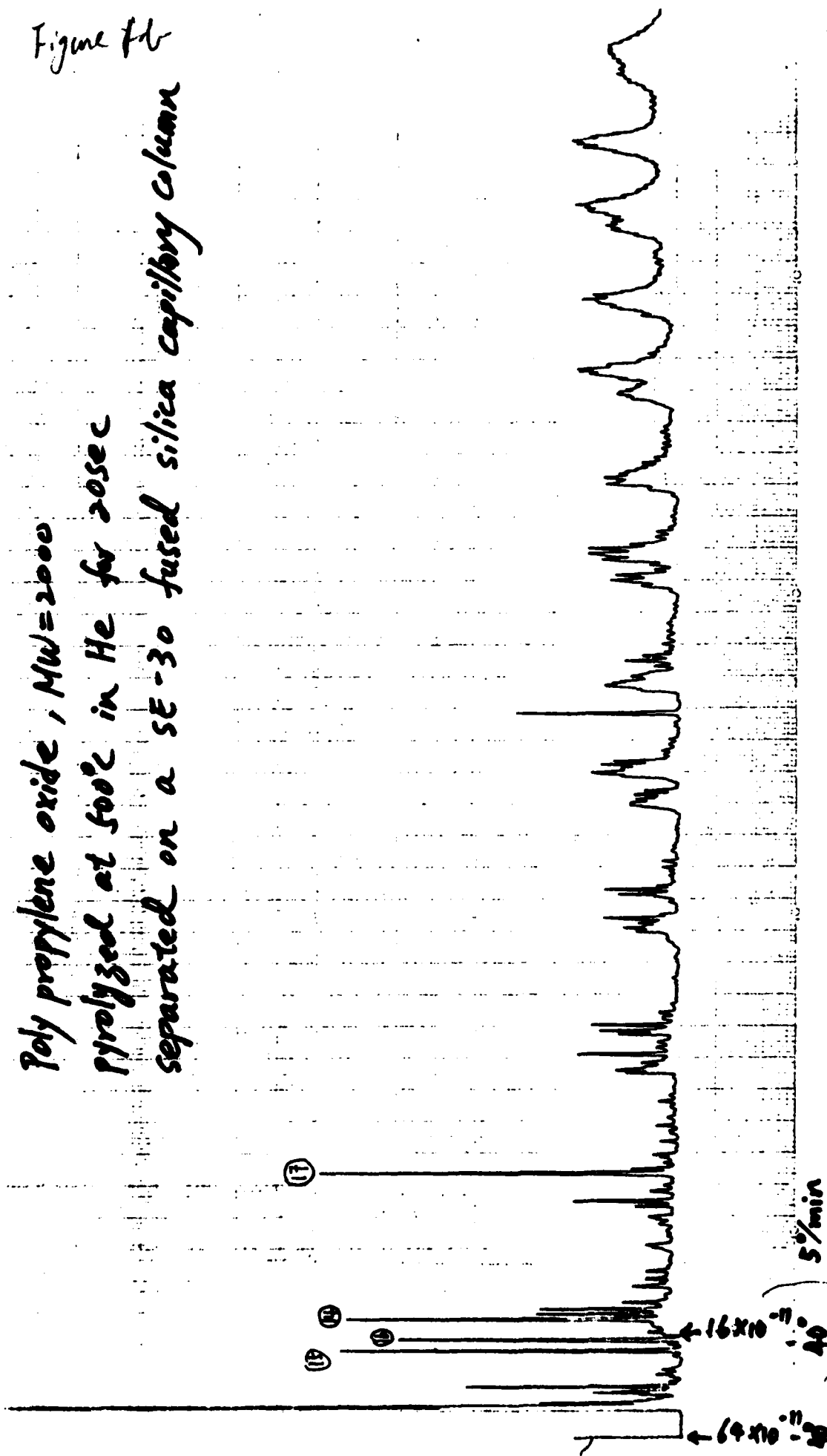


Fig 1b

11
MW = 2000

Fig 2

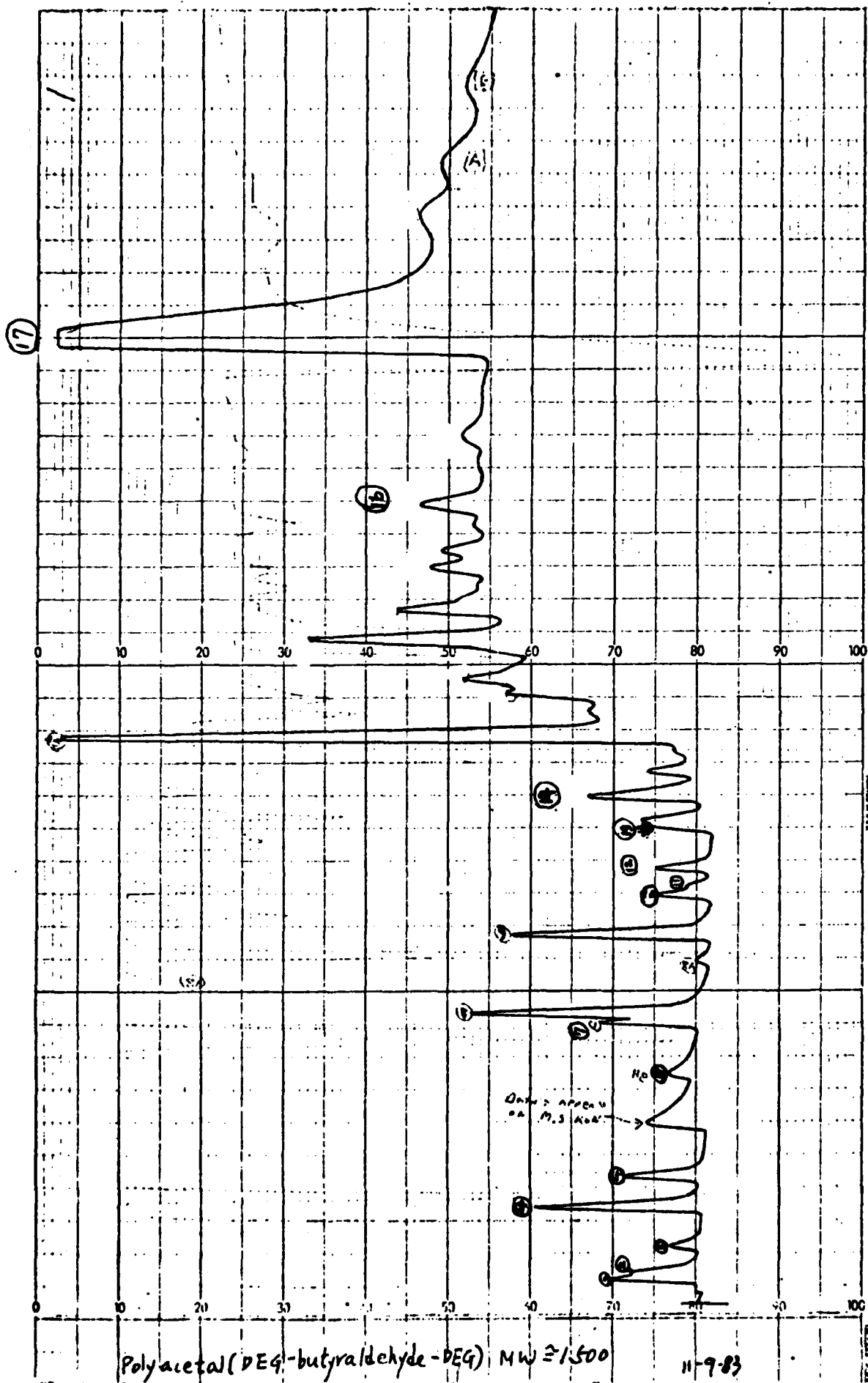
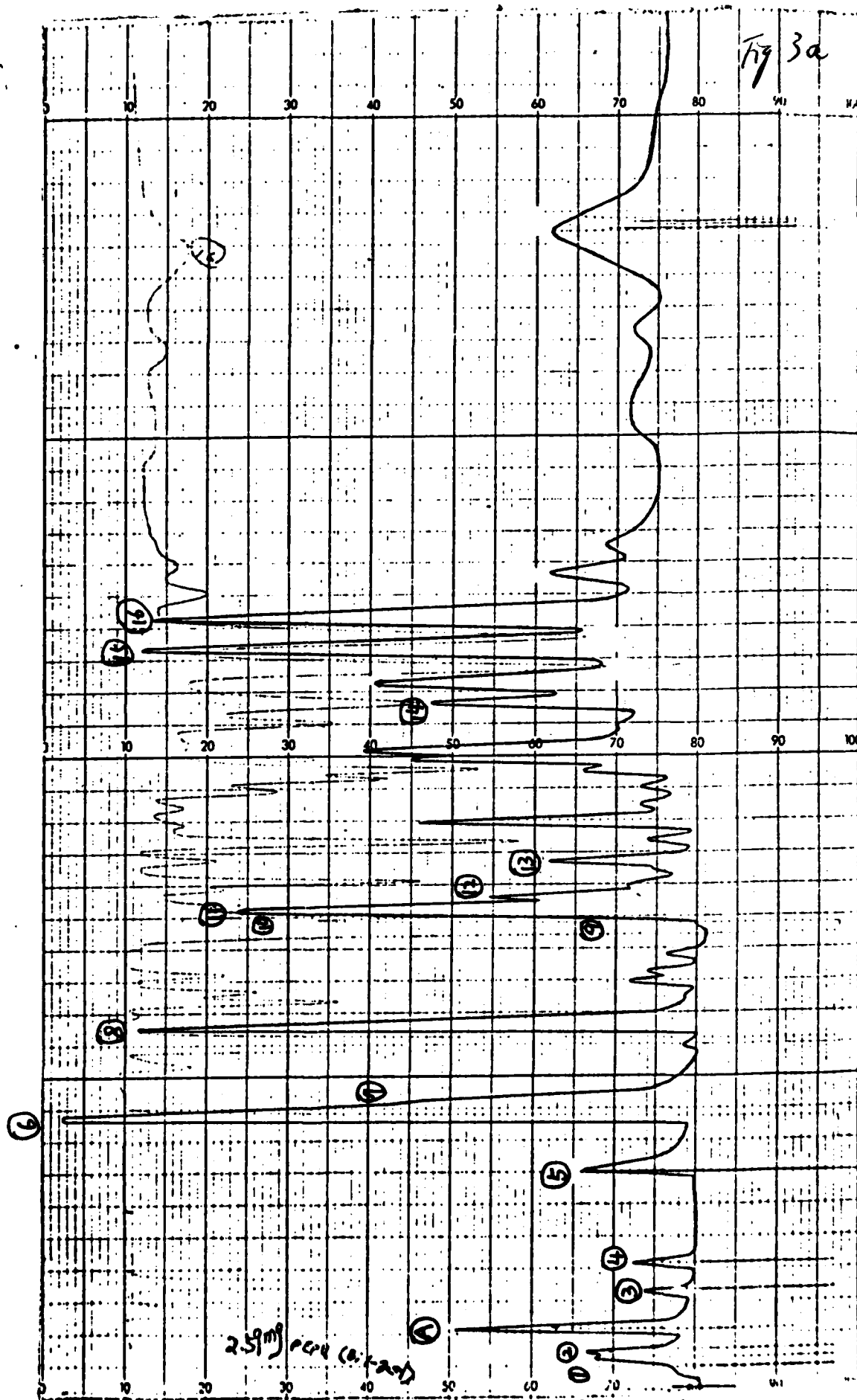
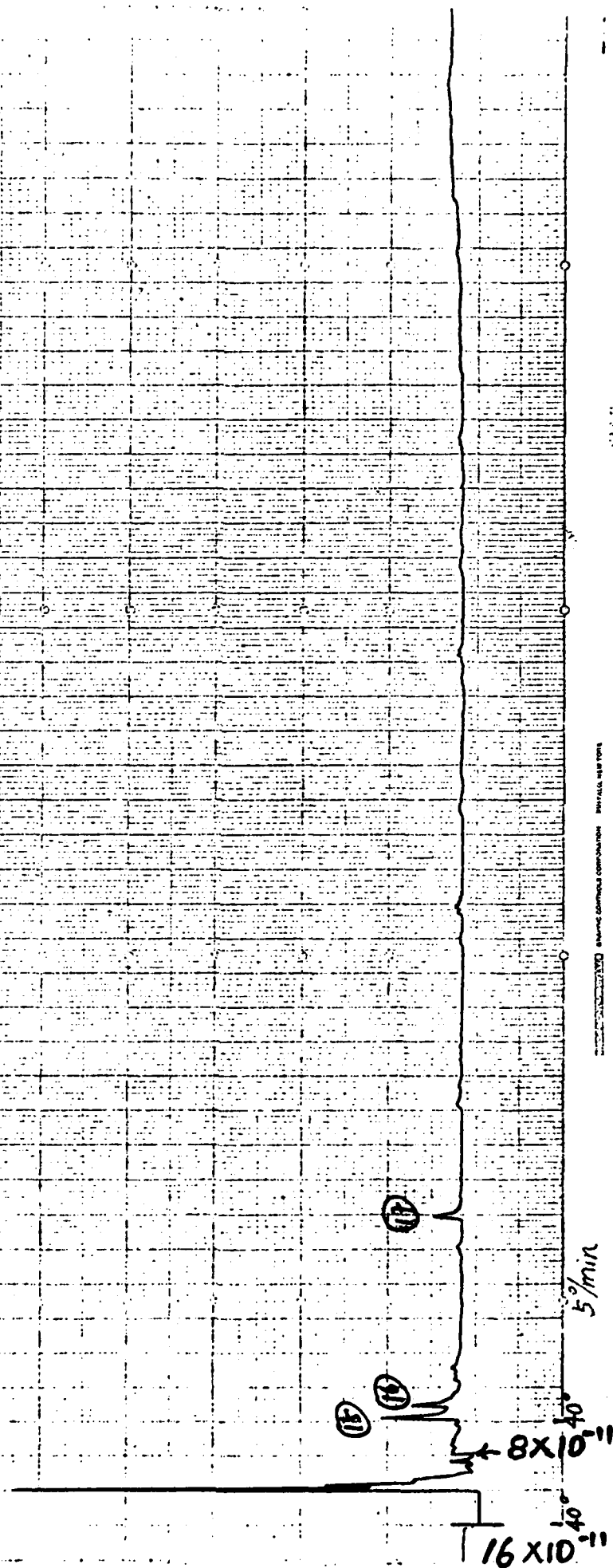


Figure 3 a



344 μ g PEPUCBi (1-2-1) (previously pyrolyzed at 330°C)
 pyrolyzed at 500°C in He for 20 sec
 separated on a SE-30 fused silica capillary column



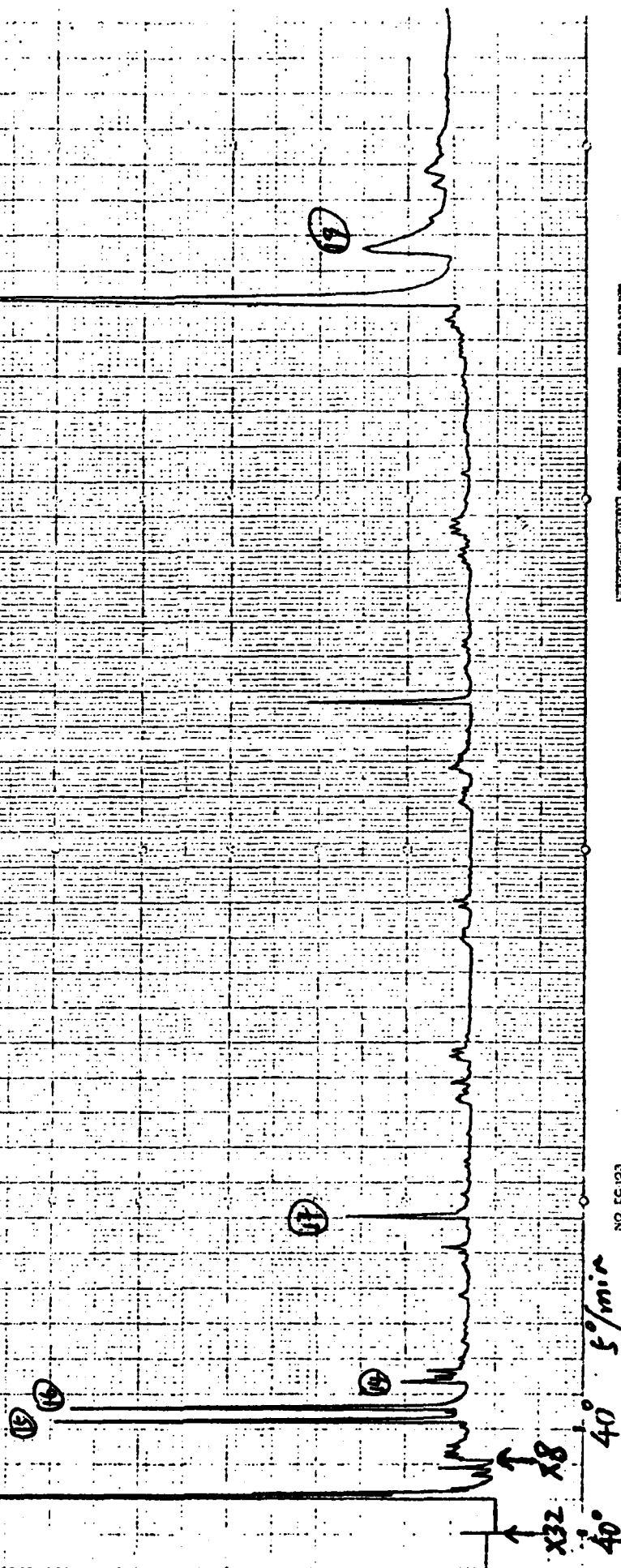
SHIMADZU MODEL 1500 CHROMATOGRAPH - DETECTOR: FID

1 Pb

219 μ g PEPX (B; 1-3-2)

Pyrolyzed at 500°C in He for 20 sec

separated on a SE-30 fused silica column



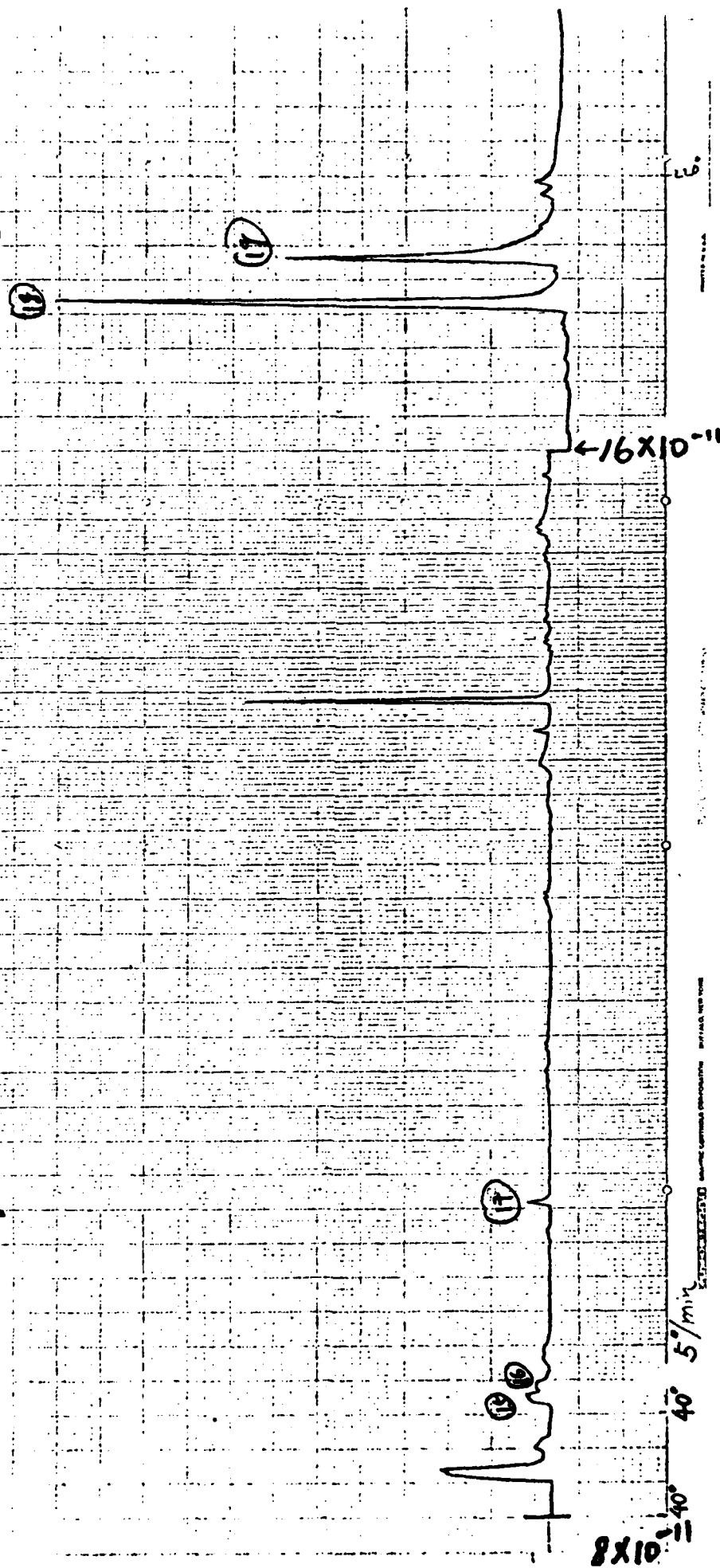
NO 60103

WATKINS-CHILCO GASTRO-SPINNING CHROMATOGRAPHY 60103A, 1000

401 μ g PEPu (S:1-3-2)

pyrolyzed at 330°C in He for 20 sec

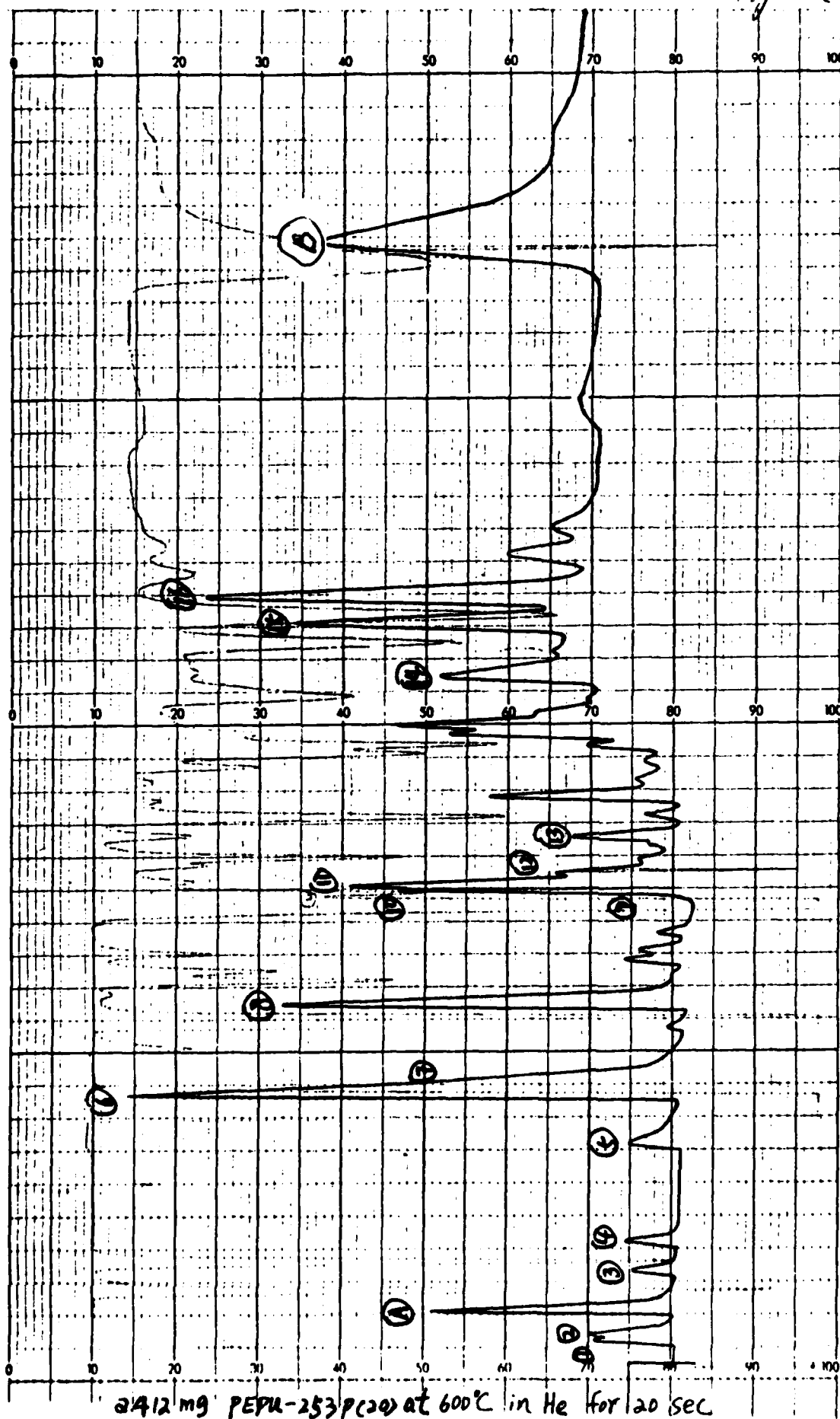
separated on a SE-30 fused silica capillary column



4a

Fig 5a

12454



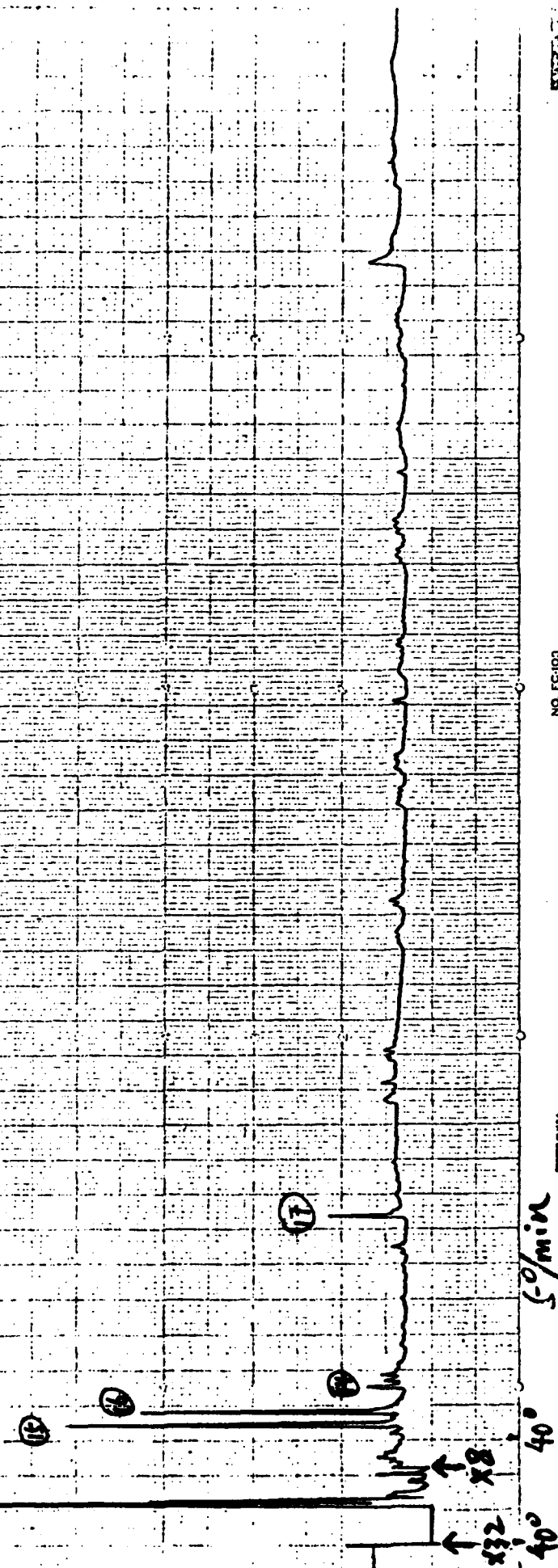
2412 mg PEPH-253P(20) at 600°C in He for 20 sec

51

176 μ g PEPIC-253 P(20)

pyrolyzed at 550°C in He for 20 sec

separated on a SE-30 fused silica capillary column



NO. EC-103

Fig 51

PPD, MW = 2000

pyrolyzed at 500°C in He for 20 sec
separated on a Carbowax-20M
fused silica capillary column

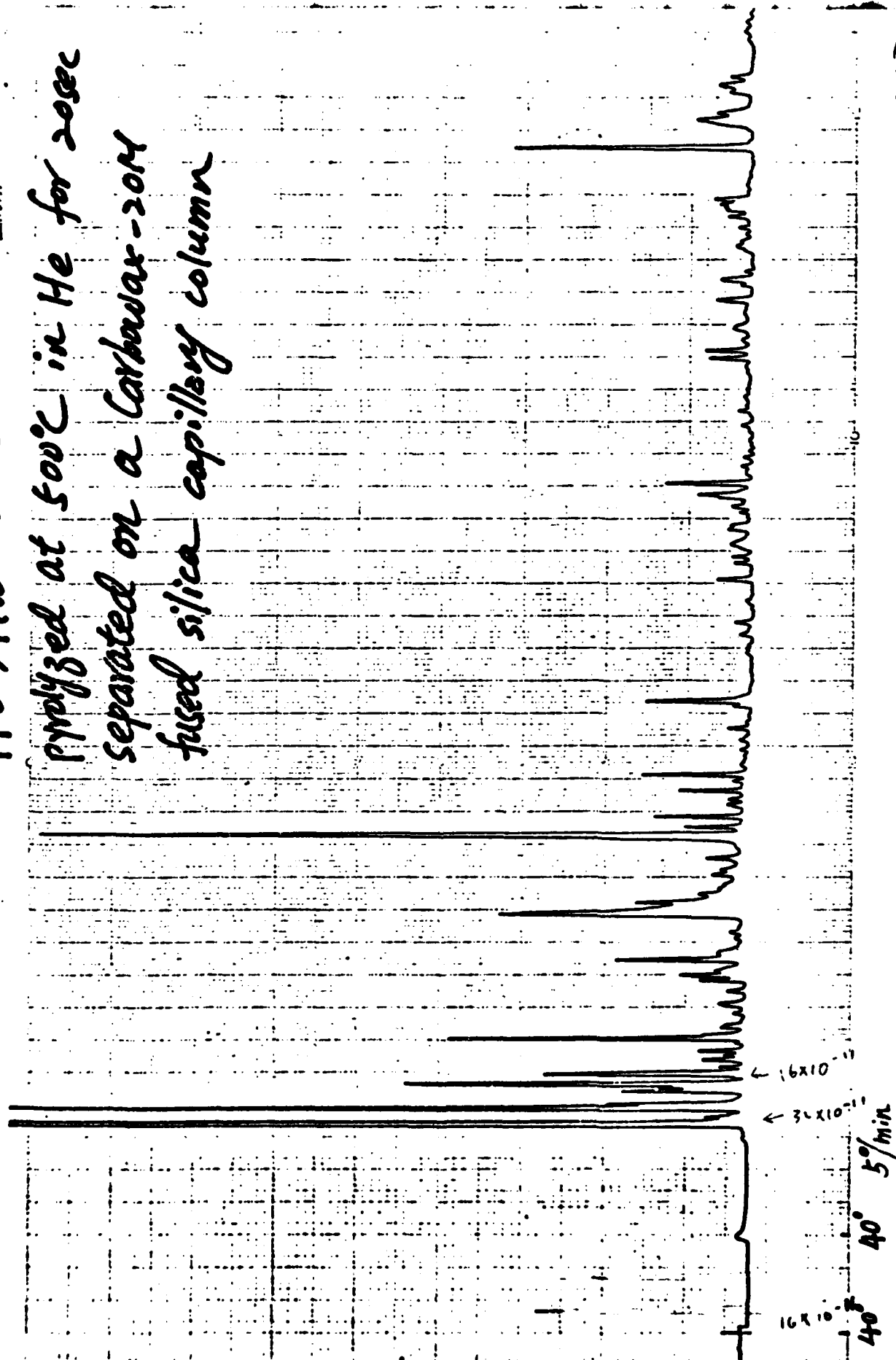


Fig 6a

555 μ g PEPI-1210 (H)

pyrolyzed at 550°C in He for 20 sec
separated on a Carbowax-20M fused silica column

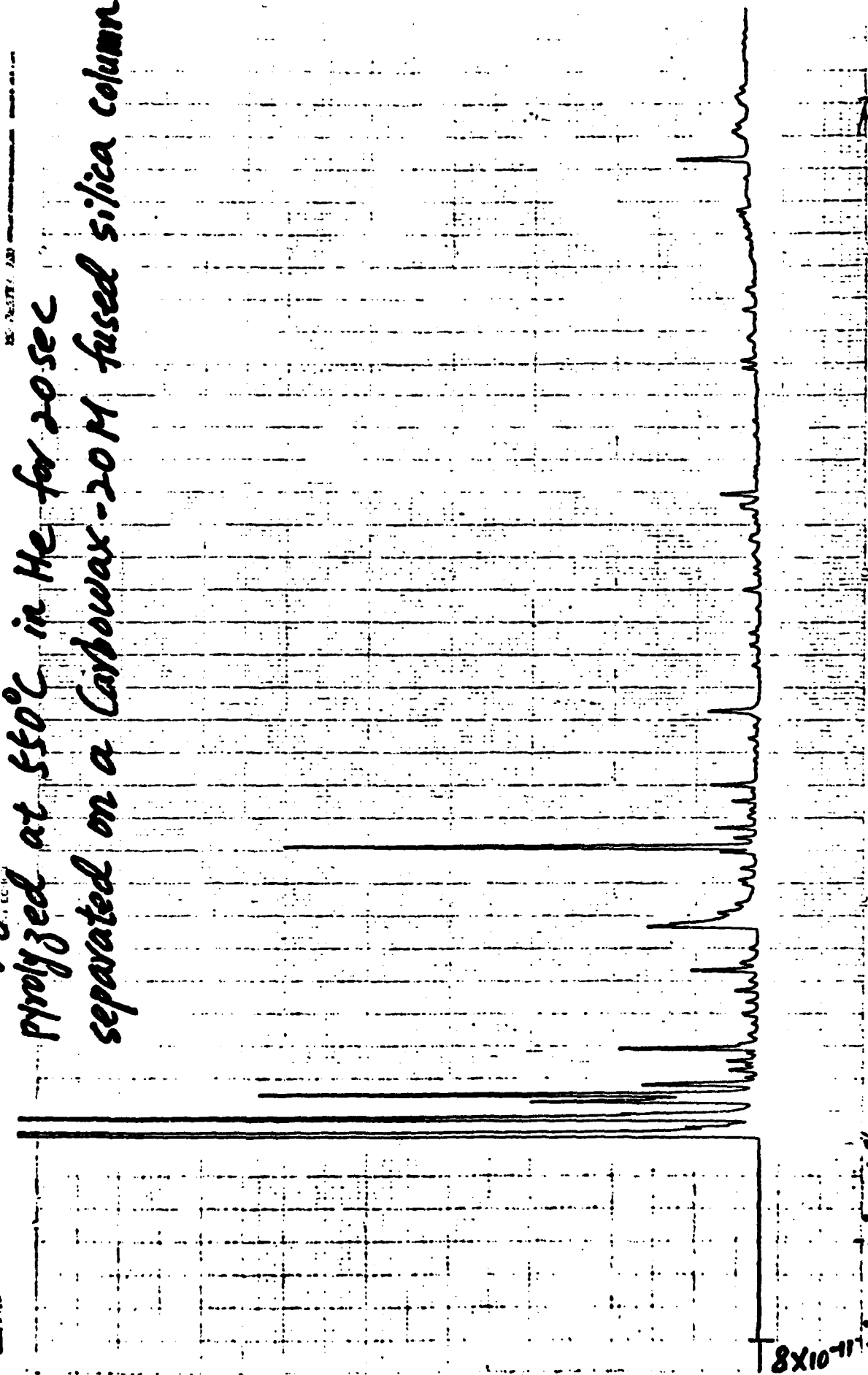
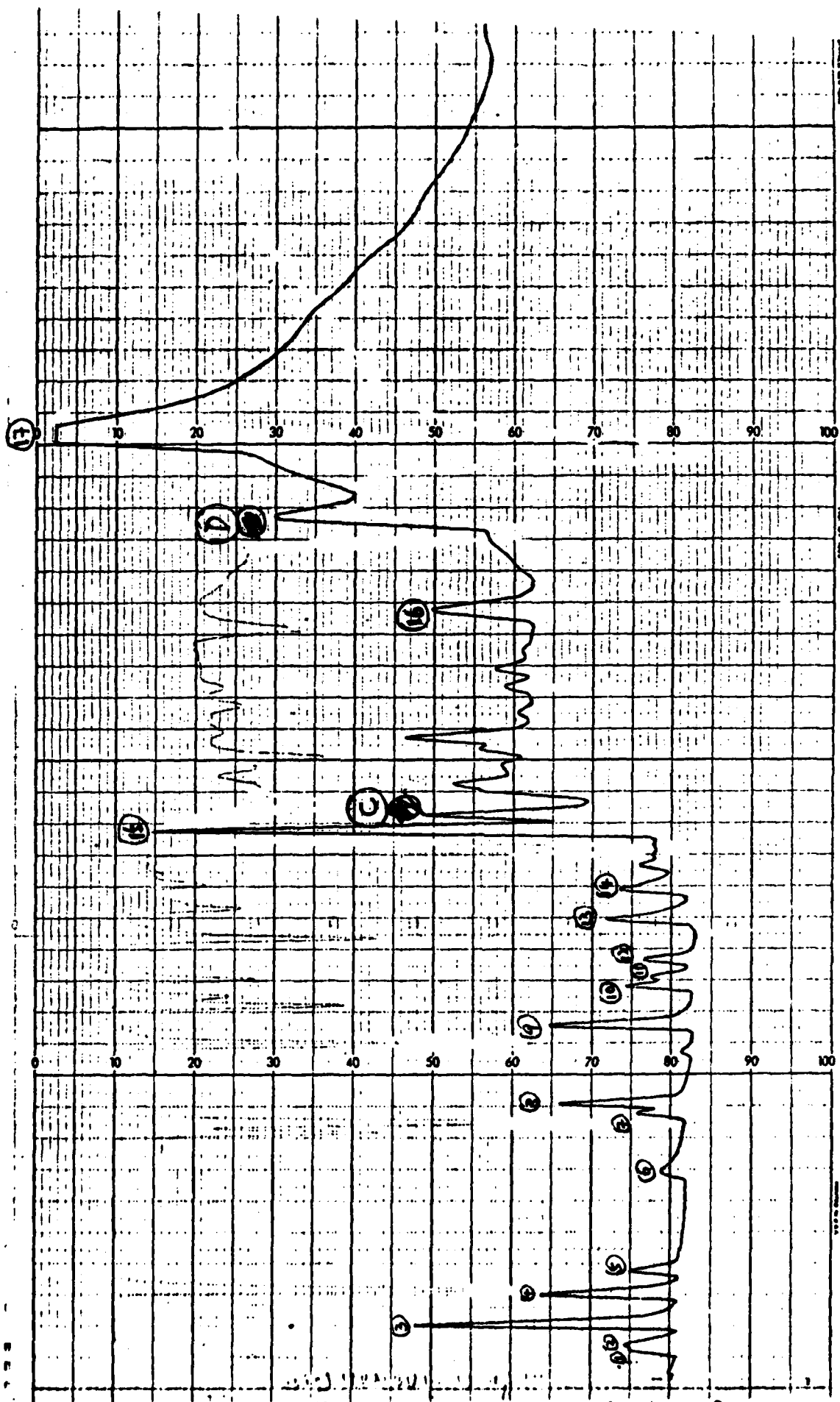


Fig. 66

Fig 1



2.158mg PAPU(BD 1-2-1) at 500°C in He for 20 sec

FILMED

9-81